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THE ACCELERATION AND RETARDATION OF THE SETTING OF PLASTER OF PARIS BY THE ADDITION OF FOREIGN SUBSTANCES

by

JOHN METSCHL

A Thesis Submitted for the Degree of

MASTER OF ARTS

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CONTENTS. PAGE

I INTRODUCTION....................1
  (a) Historical....................1
  (b) Object....................6
II EXPERIMENTAL....................6
  (a) Apparatus....................6
  (b) Method of Determining Proportions of Plaster and Water....................7
  (c) Method of Testing....................8
  (d) Materials....................10
  (e) The Influence of Colloids....................11
  (f) The Influence of Various Organic Compounds.......15
  (g) The Influence of Inorganic Acids, Bases, and Salts....................16
  (h) The Combined Effects of an Accelerator and Retarder....................20
  (i) Hardness Tests....................22
  (j) The Effect of Magnesium Oxide and Magnesium Chloride upon Plaster of Paris....................24
III THEORETICAL....................26
IV SUMMARY....................27
V BIBLIOGRAPHY....................28

INTRODUCTION.

(a) Historical.

Plaster of Paris and its uses have probably been known since prehistoric times, but the explanation of the phenomenon involved in what is commonly known as the "setting" of the plaster is far from satisfactory. The subject has been made the object of investigation by a number of the foremost investigators among whom are: Lavoisier, Marignac, Le Chatelier and van't Hoff. Each of the foregoing has contributed something towards clearing up the difficulty.

The first scientific investigation made by Lavoisier[1] related to the setting of plaster of Paris. The results of his experiments consisted of two papers, one in 1765, and the other in 1766 presented before the French Academy of Sciences. "Gypsum", said he, "is a salt formed by the union of the acid of vitriol with the earth of lime containing water of crystallization which can be driven off by a gentle heat." He said farther that "setting is simple crystallization; gypsum deprived of its water by fire reabsorbs it with avidity and again becomes crystalline. Can anything be more simple?" The august body, and the rest of the world for that matter, doubtless admitted that nothing could be more simple since Lavoisier's explanation stood for over a hundred years before it was questioned.

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[1] Lavoisier, Compt. rend., Feb. 27, 1765, and March 16, 1766; also in Oeuvres complètes, Tome III., pp. 106-144.

The man who questioned Lavoisier's explanation was one of his own countrymen, Henri Le Chatelier[1]. The latter realized that the problem was one of extraordinary difficulty, but presented an explanation which is still generally accepted today. He made use of some data collected by Marignac[2], who observed that when plaster of Paris is stirred with water, a much more concentrated solution of calcium sulphate is obtained than from powdered gypsum; the solution thus obtained being supersaturated with respect to the gypsum; in a short time deposits crystals composed of this substance. Le Chatelier then showed that the hemihydrate of calcium sulphate is readily soluble in water, and forms an unstable solution which is supersaturated with respect to the dihydrate. Particles of the latter are always present, expect in dead burned gypsum, and act as nuclei which set up crystallization of the stable dihydrate. The crystals grow in radial fashion about the numerous nuclei thus interlacing and causing the plaster to "set". This explanation accounted for the setting, but not for the expansion which takes place during the setting. W.A. Davis[3] attempted to explain this by assuming that during the setting there is a change from one crystal system, the monoclinic, to another, the orthorhombic. This change results in an expansion. C.H. Desch[4], on the other

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[1] Le Chatelier, Recherches experimentals sur la constitution des mortiers hydrauliques. 1st ed. 1887, 2nd ed. 1904.
[2] Marignac, Arch. Sci. Ph. et Nat., 48, 120, 1873 or in Oeuvres complètes, Tome II., 571.
[3] W.A.Davis, Jr. Soc. Chem. Ind. 26, 727-38 (1907).
[4] C.H.Desch, Sci. Amer. Sup. 86, 234-5 (Oct.,12, 1918).

hand, claims such an assumption is not necessary it being sufficient to assume that during the crystallization, or setting, the growing crystals press against each other which results in an expansion of the plaster. Furthermore, he claims that this explanation also accounts for the porosity of the plaster.

There is another school, however, which attempts to explain the process of setting upon a different basis. The investigations of von Weimarn[1] have shown that a solid phase separating slowly from a moderately supersaturated solution forms well-defined crystals; that separation from a highly supersaturated solution forms crystal skeletons; and the formation of a highly insoluble product in a strongly supersaturated solution gives rise to the formation of gels. The members of the new school state that the latter condition obtains in the setting of plaster of Paris. In the ordinary setting of the plaster the quantity of water is so small as to be capable of dissolving only a minute fraction of the calcium sulphate but is sufficient to form a layer of supersaturated solution around each particle of the hemihydrate. Rohland[2] suggested that the water is taken into solution in the salt in a colloidal state, but failed to present sufficient evidence to support his suggestion. The next step was a rather startling experiment performed by Cavazzi[3], who actually obtained calcium sulphate in

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[1] P.P. von Weimarn, Koll. Zeitschr. 2, 199 (1907), his papers were collected in book form, "Zur Lehre von dem Zuständen der Materie," 2 vols., Dresden, 1914.

[2] P.Rohland, Koll. Zeitschr. 13, 61 (1913).

[3] A. Cavazzi, Gazz. Chim. Ital. 42,II.71-86, or German translation in Koll. Zeitschr. 12, 196 (1913),or C.B. 84,I".1909(1913).

the colloidal state. He shook a small quantity of plaster of Paris with a relatively large amount of water and filtered the solution. To the filtrate he added an equal volume of alcohol, which caused the calcium sulphate to separate out in the form of a colloid. When subjected to a microscopic examination of 900 diameters the formation of minute, needle-like crystals was observed which grew gradually throughout the gel. This observation caused Cavazzi to advance a new explanation for the setting of plaster of Paris. He assumed that during the setting of the plaster a hydrated gel of calcium sulphate is first formed which is later gradually changed to a crystalline state by the formation of small needles. He farther sought to account for the expansion, which takes place as the plaster hardens, upon the assumption that the colloidal calcium sulphate, which first forms, contains more water than the crystalline dihydrate, so that the expansion is due to the liberation of the excess water contained in the gel. This theory accounts for at least three things: first, for the setting of the plaster, second, for the expansion, and thirdly for the presence of water which is invariably liberated as the plaster hardens. It also is in accord with the facts found through the investigations of von Weimarn just cited. The fact that Cavazzi had used alcohol to prepare his colloidal solution of calcium sulphate caused his theory to be attacked. His opponents rightly claimed that ordinaryly, alcohol is not mixed with plaster of Paris, hence the theory is unsound.

Very recently Cavazzi's theory gained additional support through a paper published by J. Traube[1], who investigated the influence of retarders and accelerators upon the setting of plaster of Paris. While engaged in this work Traube came to the same conclusions as those formulated by Cavazzi. It is of interest to note that Cavazzi's theory remained unknown to Traube until the later had completed his investigations. Traube stated that the salts of the univalent cations exert an accelerating effect which is a maximum ata concentration of approximately 0.5 N. He found that the accelerating effect decreases with the increase of the valence of the cation, and that the anions have but a small secondary influence. When the anions were arranged in a descending order they were found to correspond very closely with the Hofmeister series. Half-normal solutions of sulphuric, hydrochloric, and oxalic acids accelerated to about an equal degree, while trichloracetic and tartaric acids, of the same concentrations exerted no perceptible influence. Ortho-phosphoric, monochloracetic, acetic, propionic and citric acids of half-normal concentrations retarded the setting. Traube calls attention to the fact that this series resembles that found by investigators experimenting with hydrosols where hydrochloric acid has a very much greater coagulating power than acetic acid. From this data he concluded that the setting of plaster of Paris is of a colloidal nature; the first step in the process being the

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[1] Traube, Kolloide Vorgänge beim Binden des Gips, Struktoren in Gips; Kolloid. Zeitschf. 25, 62-66 (1919).

formation of a gel.

From all that has been said in the foregoing it is seen that Le Chatelier's theory apparently does not explain the whole process involved in the setting of plaster and that if the theory is not to be abandoned, a revision of parts of it is at least necessary.

(b) Object.

The purpose of this thesis was to find chemical compounds, or mixtures of these, which would retard or accelerate the time of setting of plaster of Paris. These compounds were to be added to the powdered plaster in the form of a solution and the time of set determined by means of the Vicat apparatus.

II

EXPERIMENTAL.

(a) Apparatus.

The instrument used to determine the time of set was the Vicat apparatus[1], sometimes also called the Vicat needle, a drawing of which is shown on the enclosed plate. The salient features of this apparatus are the cylindrical rod B, weighing 300 grams at the lower end of which is a removable, steel, cylindrical needle K, the point of which is one square millimeter in area. The brass cylinder B, is capable of being raised or lowered in the cast-iron frame A, and may be held in place by the set-screw

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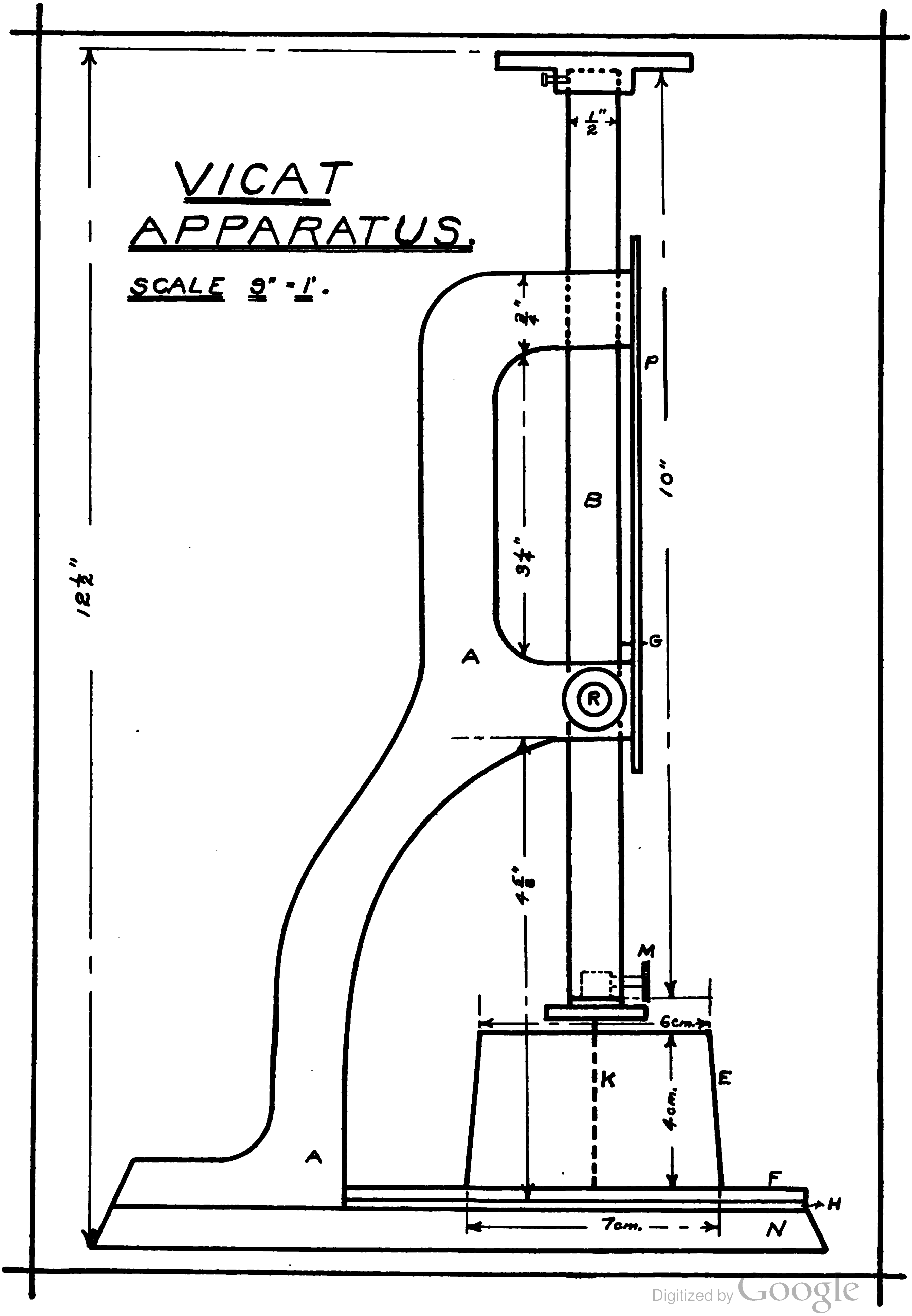
[1] For detailed description of the Vicat needle see: Concrete Plain and Reinforced by Taylor and Thompson, pp.70-72, J.Wiley & Sons, 1916; also Scott, Standard Meth. Chem. Analy. P.644.

VICAT APPARATUS.

SCALE 9" = 1'.



R. The plaster to be tested is poured into the aluminum mold E, which is in the form of a hollow, truncated cone having a base of 7cm. in diameter, an altitude of 4cm. and a diameter across the top of 6cm. The walls of the mold are about 4mm. thick.

(b) Method of Determining Proportions of Plaster and Water.

The first problem was to determine the amount of water and plaster necessary to fill the mold E. By experiment and calculation it was found that 87 grams of water required 160 grams of plaster in order to get a paste of the proper consistency. These proportions were found according to the method given in Post's Chem. Tech. Analy. Methoden[1], which with slight modifications is in brief as follows:

One hundred grams of distilled water, at room temperature, were weighed into a five-inch tared casserole. From a sheet of paper, the plaster of Paris, having the same temperature as the water, was gently but rapidly strewn into the latter until the surface of the water was no longer visible. The mass was next slightly stirred by means of a glass rod and then weighed on a platform balance which had an accuracy of 0.5g in 100 g. It would have been better to have weighed upon a torsion balance had one been available. It was found that 184 grams of plaster, had been added to the water. Hence 160 grams of plaster, enough to fill the mold, would require 87 grams of water. These proportions of plaster and water were used throughout the series.

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[1] Vol., II, pp.76-77.

of experiments which follow, To avoid the formation of lumps the plaster should be strewn into the water and not the water added to the plaster. Prolonged stirring of the plaster and water results in the formation of bubbles and is to be avoided.

(c) Method of Testing.

One hundred and sixty grams of plaster of Paris were weighed out upon a sheet of paper on the platform balance, after which 87 grams of distilled water, or the same amount of solution under investigation, were similarly weighed out in a casserole. The plaster was next rapidly strewn into the water, or solution, and slightly stirred. The time when all of the plaster had been added was recorded and taken as the beginning of the run. The mixed mass of plaster and water was then poured into the mold E, of the Vicat apparatus and any excess removed by means of a spatula which was then passed over the top of the mold to insure an even surface. The mold and its contents were then placed under the needle of the apparatus as shown in the drawing. The same procedure was carried out in all succeeding experiments.

In pouring the plaster into the mold the latter always rested upon a glass plate F, which in turn was placed upon the immovable brass plate H. The use of the glass plate made it possible to readily move the mold and plaster about under the needle when making the tests. At intervals of one minute the needle was carefully brought into contact with the surface of

the paste and then quickly released by means of the set-screw R. This procedure was continued until the needle failed to completely penetrate the mass of paste in the mold. The time when this occurred was noted. The difference in time, in minutes, between the failure of the needle to completely penetrate the plaster in the mold and the time of mixing of the plaster was called the initial set. After the initial set had been found the needle was continued to be released, at intervals of a minute, from the surface of the mold until no visible impression was made upon the surface of the cake of plaster and the time recorded. The difference in time between the time of mixing of the plaster and the failure of the needle to make any visible impression upon the mold was considered to be the final set. In all cases observed the initial set took place very sharply, and with experience in the use of the instrument, samples of the same plaster could be checked within half a minute. The final set, on the other hand, in the majority of cases is not nearly as sharp as the initial set, seldom agreeing within 2 to 3 minutes on the same specimen. In all cases the initial set is the most reliable and probable the most useful because when a mass of plaster begins to set it can be worked only with great difficulty, if at all.

In order to release the mass of hardened plaster from the mold, it was found convenient to heat the latter slightly in the flame of a Bunsen burner for a half minute or so. This

causes the mold to expand and the cake of plaster is easily removed. It also was found advisable to grease the inside and outside of the mold with a slight amount of vaseline in order to facilitate the removal of the hardened plaster.

(a) Materials.

The plaster used in this investigation was of the variety known as "dental plaster". A qualitative analysis showed that it contained as impurites small amounts of sand, together with some iron and aluminum but no organic matter. The plaster, as received, was found to be finely ground, in fact most of it easily passed through a 200 mesh sieve leaving only a small amount of sand-grains behind. Two lots of plaster were received at different times. They are known as "plaster No. 1", and "plaster No.2 in the various tables given in this investigation. For plaster No.1 the normal initial occurred in 25 minutes and the normal final set in 53 minutes. Plaster No.2 has a normal initial set of 18 minutes and a normal final set of 50 minutes. By a "normal set" is meant the number of minutes required for a cake of plaster to set without the addition of an accelerator or retarder. The initial and final sets,were of course, determined with the Vicat apparatus. The plaster was stored in tightly covered tin cans in the laboratory.

The reagents used were chemically pure, and were of the same kind as those used for quantitative analytical work in the laboratories of this university. The following exceptions are to noted:

Lithium chloride appeared to have taken up considerable moisture, and the agar-agar contained impurities in the form of straw and hence some of the determinations made with this substance are out of agreement.

"Sapo-Venatus", given in Table I(a), is a pure, powdered soap used in water analysis. The Ivory Soap used was also in the form of a powder, but ought to have been dried in a dessicator as some moisture was present.

"Certus glue", given in Table I(b), is a casein, waterproof cement sometimes used to hold the sections of an aeroplane propeller together.

The emulsion, in the same table, consisted of two grams of gum arabic , 16cc. of kerosene and 30cc. of water which were vigorously shaken together in a dry bottle. Ten and 20cc. of this emulsion were respectively diluted 87cc. with water and the effect upon the setting observed.

Distilled water was used in all determinations. It was kept in the laboratory in glass-stoppered bottles. The temperature of the water was the same as that of the plaster.

(e) The Influence of Colloids.

The list of substances given in tables I(a) and I(b) is usually classed as colloidal. With the exception of the soaps and the emulsion, all of these retarded both the initial and final setting of the plaster. A one percent solution of agar-

agar added to the plaster made an exceedingly thick paste which was poured into the mold with difficulty. The paste resembled a dough and could be formed into tubes and various other objects by hand. These same properties were observed by other investigators[1] in the case of pulverized marshmellow root.

The principal retarders of this group are gelatine, marshmellow root, certus glue and agar-agar. Gelatine is doubtless the best retarder of this class and is frequently used as such in the technical arts. None of the retarders discolored the plaster and also apparently did not diminish its strength. Hain,[2] Greisenauer,[3] and Sherman[4] have shown that the presence of organic matter and clay had little or no effect on the tensile strength of mortar and concrete, in fact in one case[5] the washing out of the loam decreased the tensile strength. The same is probably true for plaster of Paris.

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[1] A. Astruc and Juillet, Jr. Pharm, et Chim. (7) 9, 5-19, abstracted in C.B. 85, I' 740 (1914).

[2] Eng. News, 53, 127 (1905).
[3] ibid. 51, 413 (1904).
[4] ibid. 49, 443 (1903).
[5] ibid. 49, 446 (1903).

Abbreviations Used in the Tables That Follow.

Conc.	Concentration of compound used with the plaster.
t.I.Set	Time, in min., required for the initial set.
t.F.Set	" " " " " " final " .

A retardation of the initial or final set is indicated by a minus sign before the number of minutes. When no sign is given an acceleration is implied.

TABLE I(a).

Colloids.

Determinations made with plaster No. 1.

Compound	Conc.	t.I.Set	t.F.Set	Effect on I.Set	Effect on F.Set
Agar	0.23%	39 min.	166 min.	-14 min.	-113 min.
"	0.75	48	62	-23	-9
"	0.75	44	61	-19	-8
"	0.75	41	56	-16	-3
"	1.00	49	58	-24	-5
Gelatine	0.75	More than six hours.			
"	0.15	95	131	-70	-78
"	0.15	79	123	-54	-70
"	0.15	78	127	-53	-74
Glucose	1.00	31	62	-6	-9
Gum arabic	0.15	28	64	-3	-11
Dextrin	1.00	38	63	-13	-10
Sol.Starch	1.00	39	53	-14	0
Sapo Venatus	1.00	23	38	2	15
" "	0.75	29	49	-4	4
Ivory Soap	1.00	17	27	8	26
" "	0.75	29	40	-4	13
Marshmellow root	1.00	65	97	-40	-44

TABLE I(b).

Colloids.

Determinations made with plaster No.2.

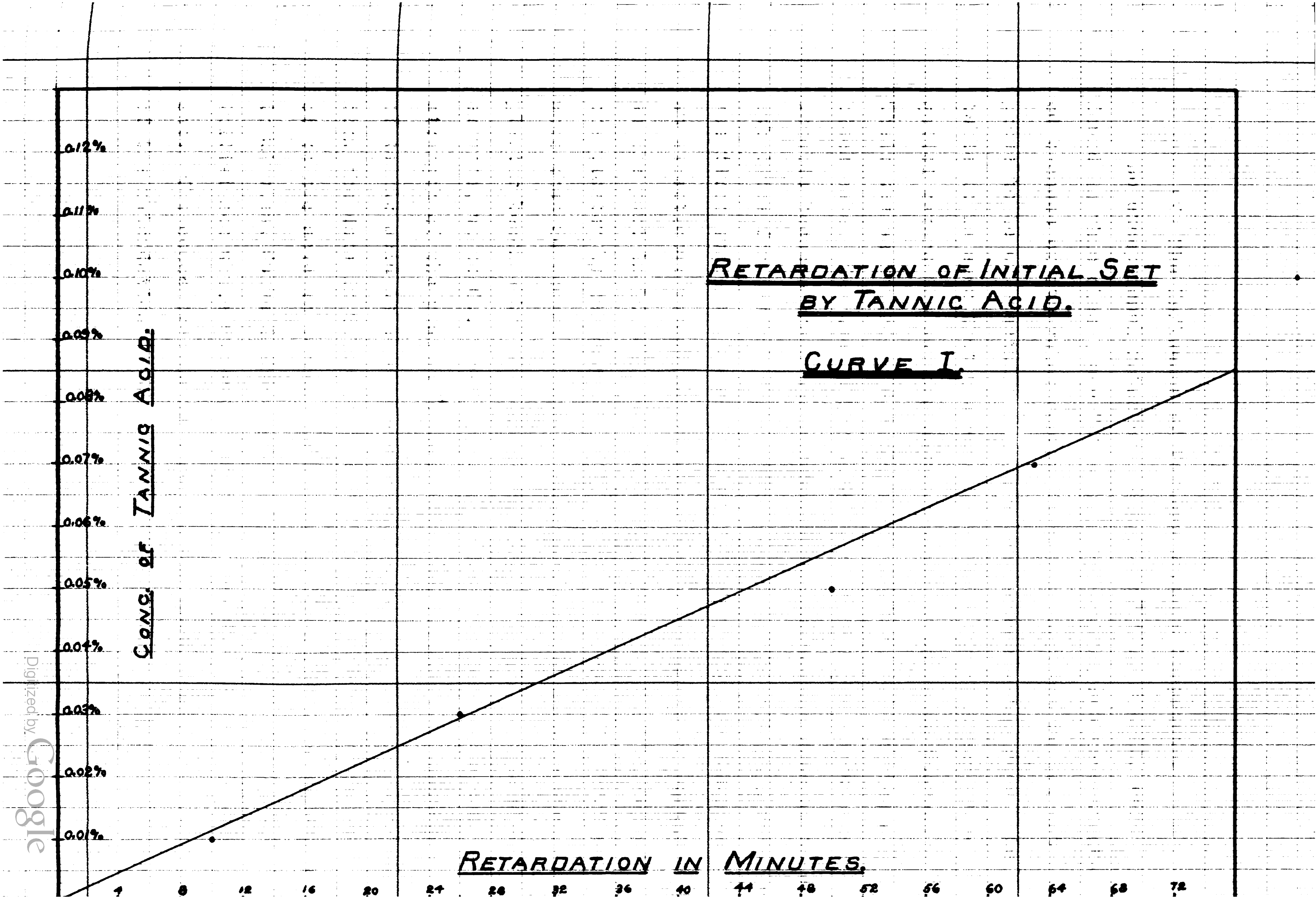
Compound	Conc.	t.I.Set	t.F.Set	Effect on I.Set	Effect on F.Set
Egg albumen	0.15%	20 min.	53 min.	-2 min.	-3 min.
Emulsion	10cc.	15	44	3	6
"	20cc.	12	34	6	16
Certus glue	1.0%	56.5	148	-38.5	-98

TABLE II.

Various Organic Compounds.

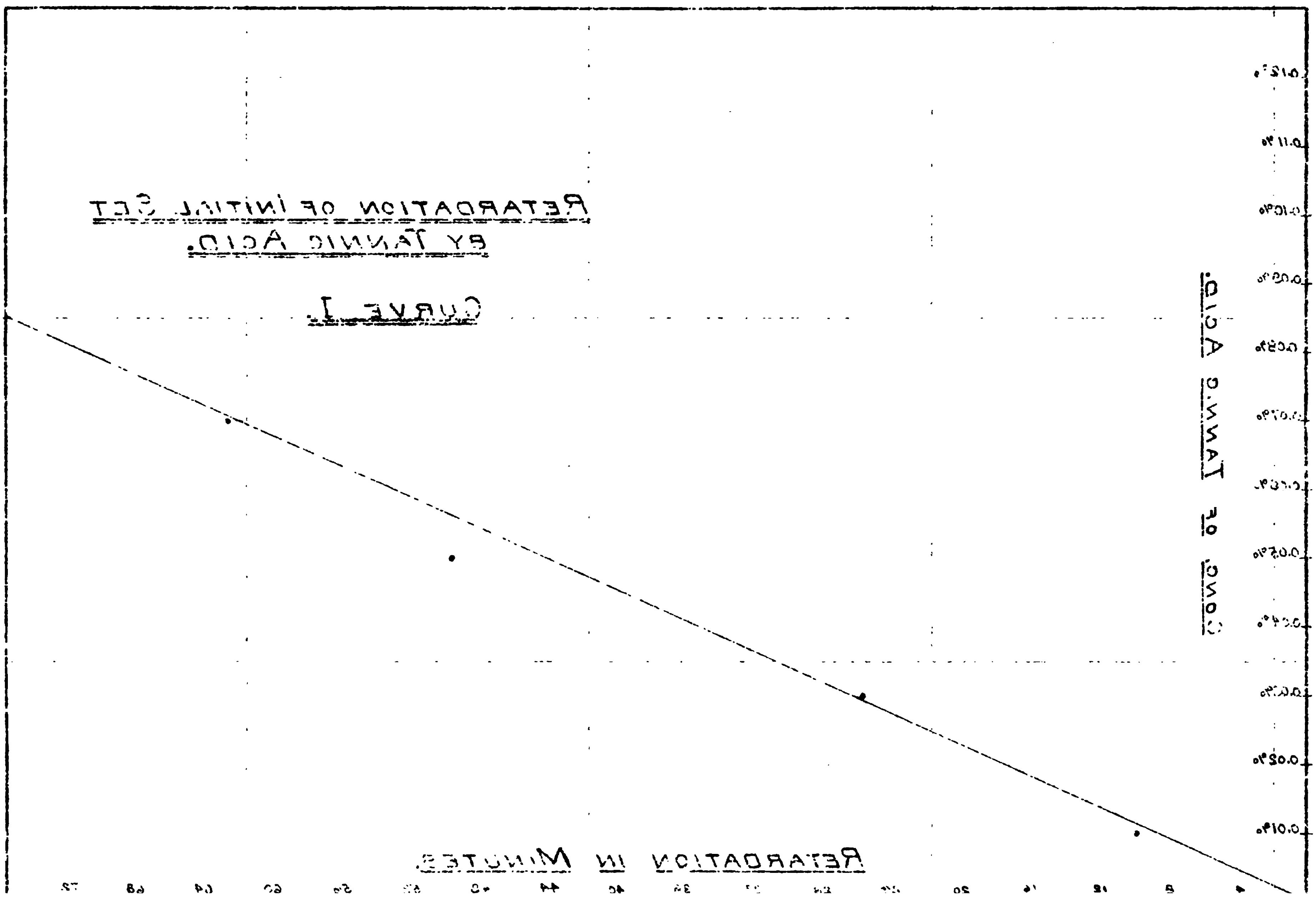
Determinations made with plaster No. 1.

Compound	Conc.	t.I.Set	t.F.Set	Effect on I.Set	Effect on F.Set
Pyridine	5cc.	45 min.	85 min.	-20 min.	-32 min.
Catechol	0.75%	40	63	-15	-10
Pyrogallol	0.75	44	92	-19	-39
Sucrose	1.00	35	60	-10	-7
Tannic acid	0.01%	35	62	-10	-9
"	0.03	51	85	-26	-32
"	0.05	75	100	-50	-47
"	0.07	88	114	-63	-61
"	0.10	103	136	-78	-83
"	0.15	182	225	-157	-172
"	0.75	Final set retarded more than 24 hours.			



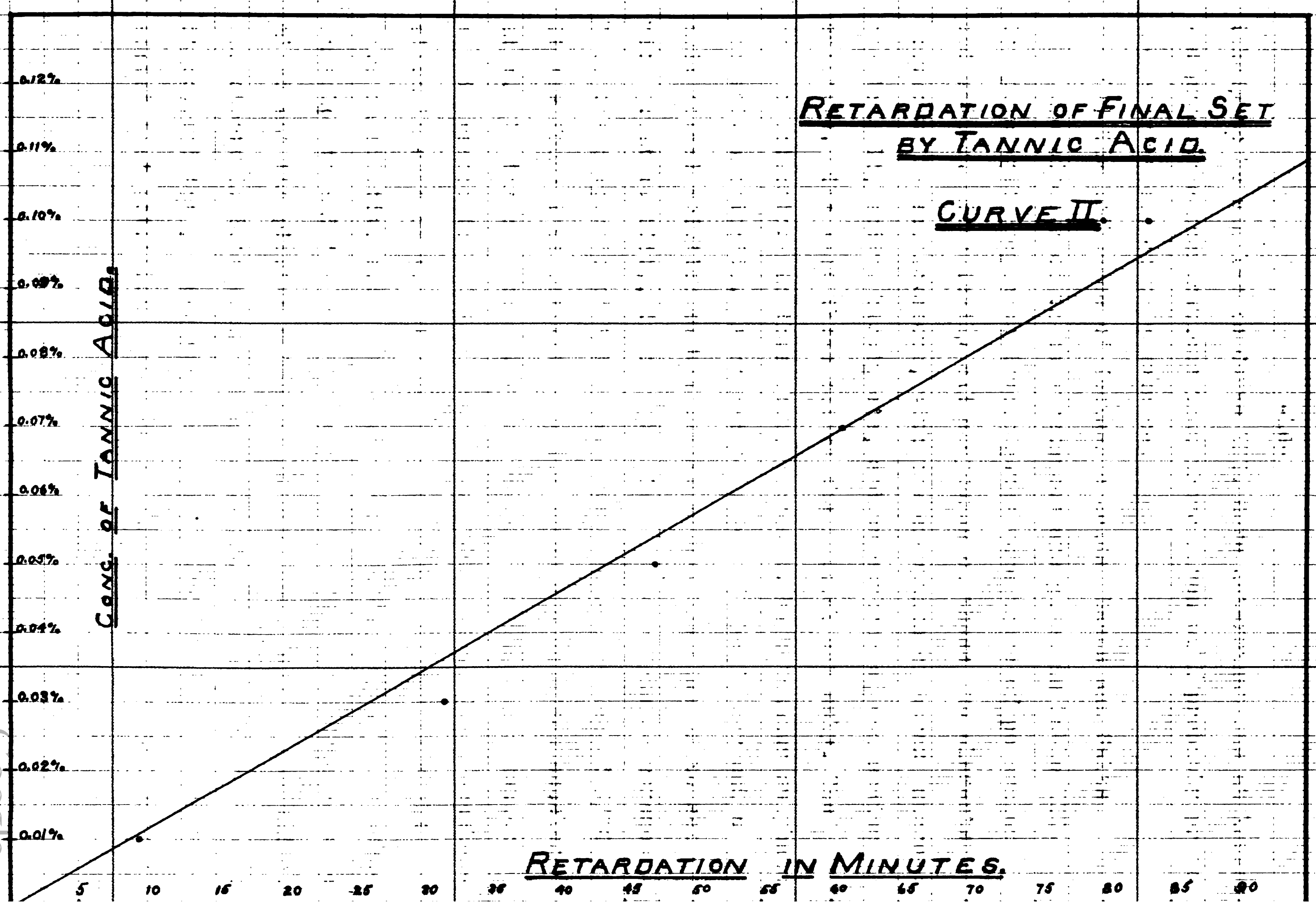
RETARDATION OF INITIAL SET BY TANNIC ACID.

CURVE I.


RETARDATION OF INITIAL SET
BY TANNIC ACID.
CURVE I.
CONC. OF TANNIC ACID.
RETARDATION IN MINUTES.
0.01%
0.02%
0.03%
0.04%
0.05%
0.06%
0.07%
0.08%
0.09%
0.10%
0.11%
0.12%
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72

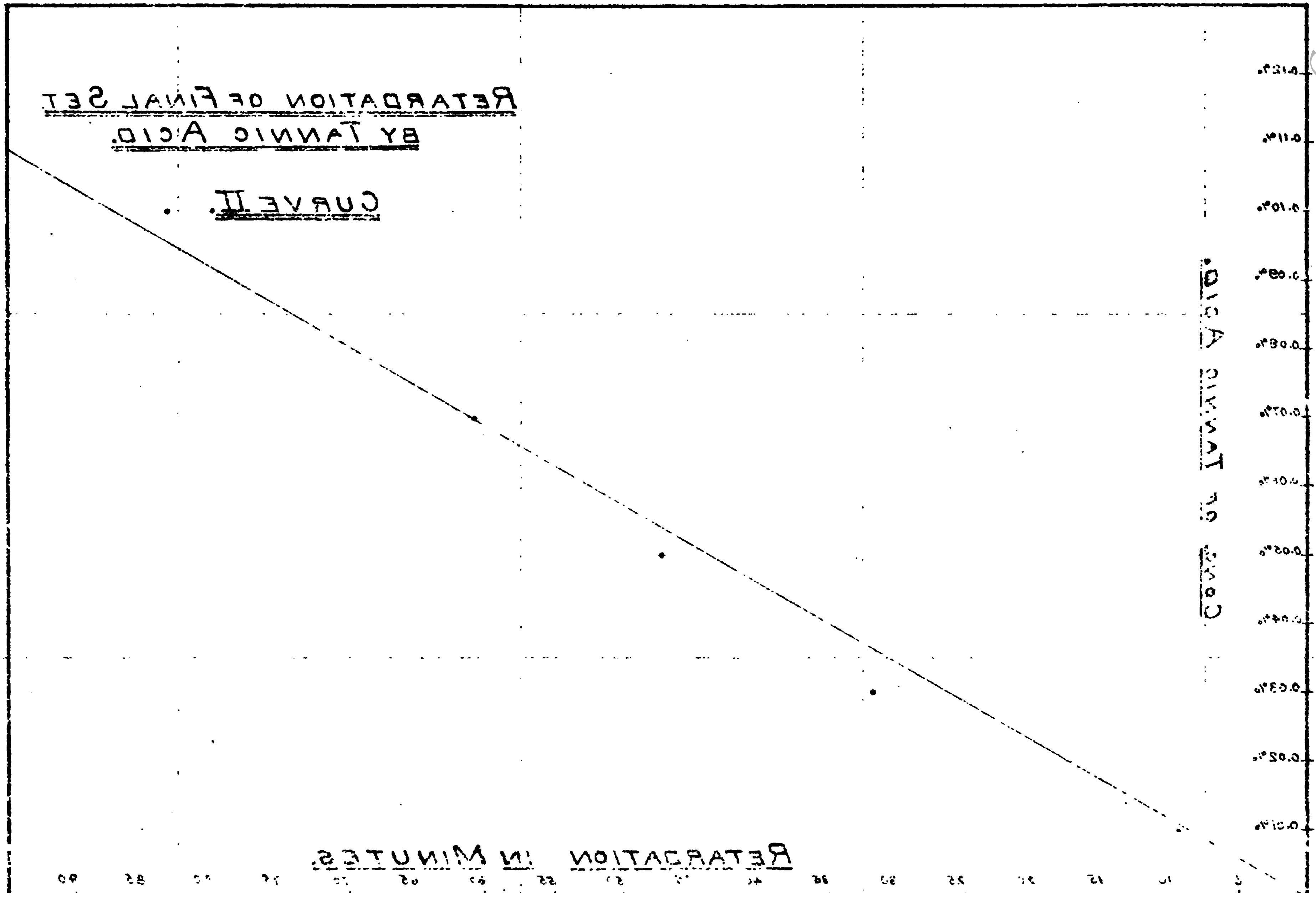
(f) The Influence of Various Organic Compounds.

No exceptional retarders, outside of tannic acid, were found in this class, see Table II. Pyrogallol was investigated because of its relationship to tannic acid but it did not prove to be of special value as a retarding agent. From this table it is seen that the same amounts of catechol and pyrogallol retard the setting approximately to an equal degree. Their use as retarders discolors the plaster, both giving a black cake. The use of pyridine in plaster might prove objectionable because the plaster retains the unpleasent odor of this substance for several days. The use of tannic acid as a retarder was first suggested by Dr. Walton. It was found to exercise an exceptional retarding influence. Even as small an amount as one part in 10,000 were found to retard the initial set of the plaster by ten minutes, while 0.75% retarded the final set more than 24 hours. In concentrations as high as this the plaster becomes brittle and discolored when dry, but in small amounts, up to 0.15% and higher, neither the color nor the strength of the plaster appear to be effected. The influence of tannic acid is shown graphically in Curves I andII, plotted from the data in Table II. In both curves the concentrations of tannic acid in percent were plotted against the retardation in minutes. Curve I shows graphically the retardation of the initial set while Curve II shows the same thing for the final set. The concentration is probably not a straight line function of the retardation as is shown in these two curves but is more



RETARDATION OF FINAL SET BY TANNIC ACID.

CURVE II.


RETARDATION OF FINAL SET
BY TANNIC ACID.
CURVE II.
CONC. OF TANNIC ACID.
RETARDATION IN MINUTES.
0.01%
0.02%
0.03%
0.04%
0.05%
0.06%
0.07%
0.08%
0.09%
0.10%
0.11%
0.12%
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90

likely to be similar to Curve III. More determinations at lesser and greater concentrations than those given will probably prove the correctness of this surmise.

(g) The Influence of Inorganic Acids, Bases and Salts.

The effects of these substances are given in Table III. The principal compounds investigated were those of potassium and sodium. Practically all compounds of these two elements proved to be accelerators, with the exception of borax, microcosmic salt, sodium bisulphate, sodium carbonate, and sodium sulphite. The last three retard the initial set only. The best accelerators in this class proved to be potassium sulphate and sodium chloride. A normal solution of the former and a half normal solution of the latter caused the plaster to set with great rapidity, in fact too fast for accurate measurement. When the compounds of this class had a concentration of N/10 it was found that potassium sulphate was the greatest accelerator. In the case of sodium chloride when the concentration was increased from 0.10% to 1%, there was but a slight acceleration in each case. It was thought that accelerators might have an additive effect so 43.5g of a solution of N/10 potassium sulphate and the same amount of N/10 potassium nitrate, were mixed and the plaster added to the mixture. No additive effect was observed. Potassium chromate also is a good accelerator but it colored the plaster yellow. From Table III it will be observed that potassium compounds accelerate to a greater degree

than the corresponding sodium compounds. At a concentration of N/10 aluminum choride retarded both the initial and final set of the plaster. In all the papers of P. Rohland[1] this salt is always classed as an accelerator. Rohland probably based his conclusions upon his observation that accelerators are substances which increase the solubility of gypsum and the retarders are those which diminish the solubility. Unfortunately he described neither the method by which he tested his plaster, nor the concentration of his aluminum chloride solution. The concentration is of deceided importance as was found by J. Traube[2]. Mercuric chloride and cupric chloride formed discolored cakes. In the case of cupric chloride a layer of metallic copper formed at the points were the aluminum mold of the Vicat apparatus had been in contact with the wet plaster. Boric acid retarded to a less degree than was suspected since borax is quite a decided retarder. The of the latter has been known for some time; it being a retarder for mortar, cement and plaster. A greater retarder than borax is microsmic salt, its use as such being protected by a German patent.[3]

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[1] P. Rohland, Zeitschf. f. anorg. chem., 32,438 (1902); see also Zeitschf. f. elekro. chem., 14, 42 (1908).

[2] loc. cit.

[3] Hans Mendheim, D.R.P. Kl.78c. No.198284 (1903).

TABLE III.

Inorganic Acids, Bases and Salts.

Determinations made with plaster No. 2.

Compound	Conc.	t.I.Set	t.F.Set	Effect on I.Set	Effect on F.Set.
K_2SO_4	N/1	Sets in less than ½ min.			
"	1%	4 min.	11 min.	14 min.	39 min.
"	N/10	5	14	13	36
K_2SO_4 & KNO_3	N/10	5.5	12.5	12.5	37.5
K_2CrO_4	N/10	6	12	12	38
KNO_3	N/10	6	13	12	37
KCl	N/10	6.5	17	11.5	33
KBr	N/10	7.5	13.5	10.5	36.5
KI	N/10	7	23	11	27
KI	1%	8	23	10	27
$KClO_3$	N/10	10	25	8	25
K_2S	N/10	12.5	28.5	5.5	21.5
K_2CO_3	N/10	15	31	3	19
$KHSO_4$	N/10	15	28	3	22
NaCl	N/2	Sets in less than 2 min.			
"	N/10	9	25	9	25
"	0.10%	16	47	2	3
"	0.15%	12	40	6	10
"	0.15%	13	40	5	10
"	0.20%	12	35	6	15

TABLE III.
(continued)

Compound	Conc.	t.I. Set	t.F.Set	Effect on I.Set	Effect on F.Set
NaCl	0.20%	13 min.	41 min.	5 min.	9 min.
"	0.20%	13	37	5	13
"	0.30%	13	32	5	18
"	0.50%	10	28	8	22
"	0.75%	10	23	8	27
"	1%	8	20	10	30
"	1.5%	6	19	12	31
"	2%	5	17	13	33
$Na_2B_4O_7$	1%	45	143	-27	-93
Na_2SO_4	N/10	9	18	9	32
NaCN	N/10	13.5	36	4.5	14
$NaHSO_4$	N/10	20	39	-2	11
$NaNO_2$	N/10	11	27.5	7	22.5
Na_2SO_3	N/10	22	45	-4	5
Na_2CO_3	N/10	23	49	-5	1
$NaNH_4HPO_4$	1%	66	226	-43	-173
NaBr	N/10	8	28	10	22
$BaCl_2$	N/10	17	47	1	3
$HgCl_2$	N/10	19	49	1	1
$CuCl_2$	N/10	13	31	5	19
LiCl	N/10	13	40	5	10
$AlCl_3$	N/10	22	56	-4	-6
"	N/10	23	61	-5	-11
$CaCl_2$	N/10	16	39	2	11
$FeCl_3$	N/10	24	47	-6	3
$MgCl_2$	N/10	16	36	2	14
$ZnSO_4$	1%	15	46	3	4
H_3BO_3	N/10	20	49	-2	1
K_2SO_4 & H_3BO_3	N/10	8	23	10	27

(h) The Combined Effects of an Accelerator and Retarder.

The data in Table IV. gives the results obtained by combining the retarder tannic acid, with an accelerator, potassium sulphate. Forty-three and one-half grams of tannic acid having a concentration of one part acid to 1000 parts of water, were mixed with the same weight of N/1 potassium sulphate. To the 87 grams of this mixture the plaster was added and the initial and final sets were observed. The same procedure was repeated with N/2, N/4, N/8, N/16, N/32 and N/64 potassium sulphate, the tannic acid always having the same concentration as in the first case, namely one part of acid in 1000 parts of water. From the data so obtained Curve III was plotted, here the concentration of the potassium sulphate is plotted against the retardation of the initial set. It is seen as the concentration of the potassium sulphate is decreased the curve descends to the left and crosses the zero ordinate at a concentration a little below N/8, at this point the effects of the tannic acid and potassium sulphate neutralize each other. After crossing the zero ordinate the tannic acid plays the predominant part, and if the dilution of the potassium sulphate had been continued to infinity the curve would have intersected the x-axsis at -44, that being the retardation, in minutes produced by a solution of tannic acid of a concentration of 1 to 1000 without the presence of potassium sulphate. It is impossible, of course, to obtain such a condition in actual practise because there would

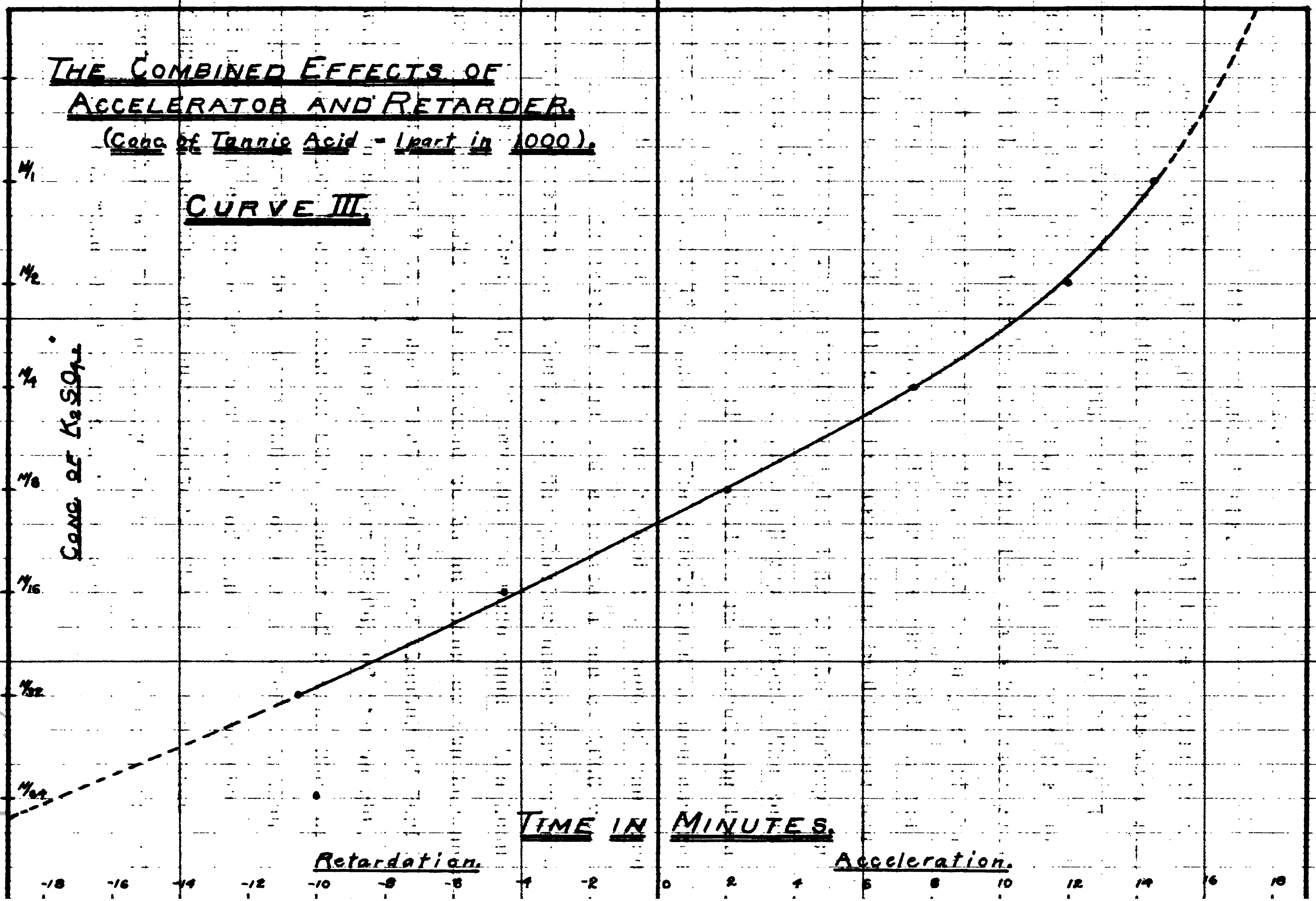
be some potassium sulphate present no matter how great the dilution.

TABLE IV.

The Combined Effects of an Accelerator and Retarder.

Determinations made with plaster No. 2.

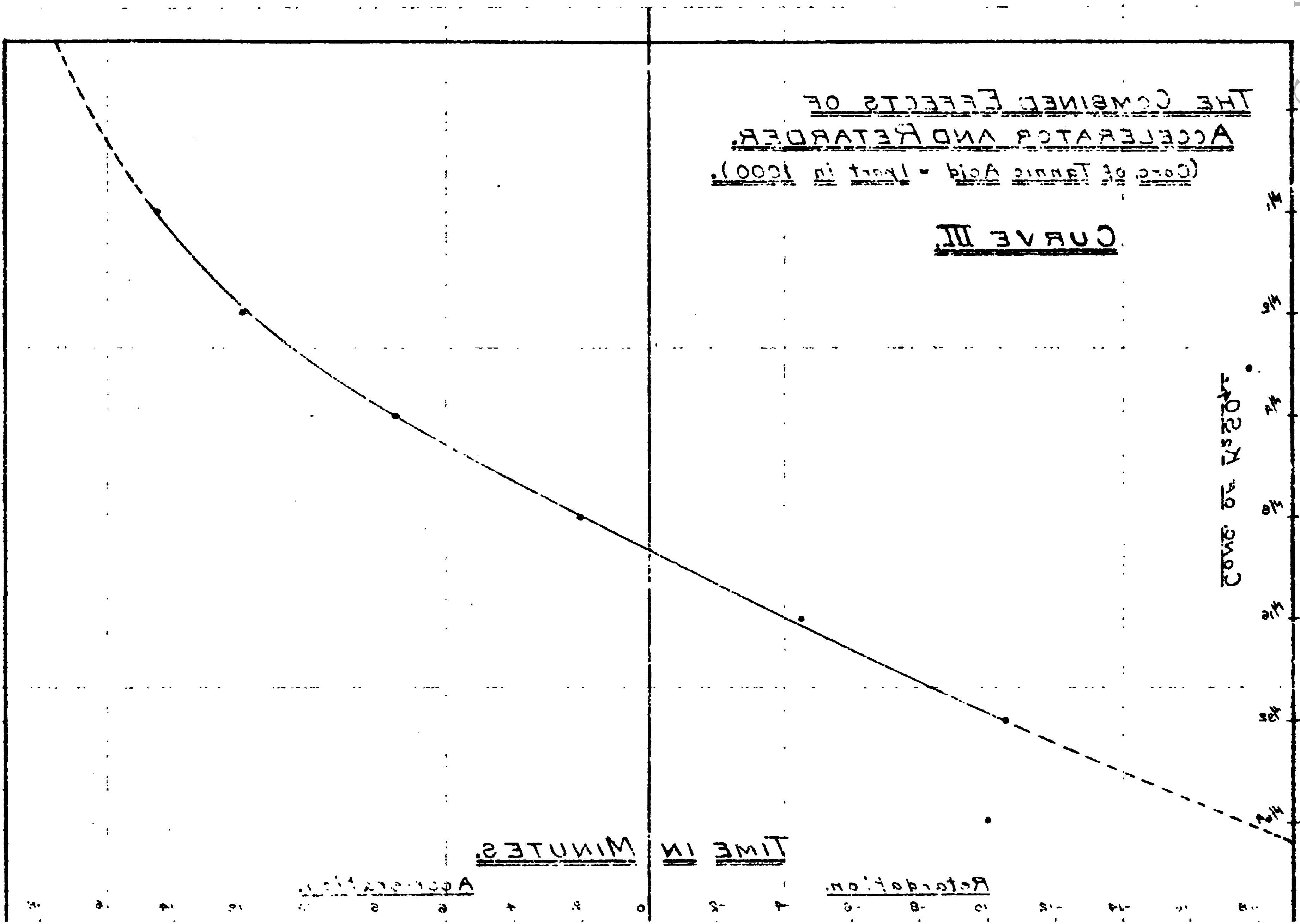
Compound	Conc.	t.I.Set	t.F.Set	Effect on I.Set	Effect on F.Set
K_2SO_4&tan.acid	N/1	3.5min.	7min.	14.5min.	43min.
"	N/2	6	13	12	38
"	N/4	10.5	17	7.5	33
"	N/8	16	29	2	21
"	N/16	22.5	43	-4.5	7
"	N/32	28.5	50	-10.5	0
"	N/64	27	60	-9	-10
"	N/64	25	55.5	-7	-5.5
"	N/64	28	60	-10	-10
Tannic acid alone	1 to 1000cc H_2O	62	113	-44	-63
K_2SO_4	N/1	Sets in less than ½ minute.			



THE COMBINED EFFECTS OF ACCELERATOR AND RETARDER.

(Conc. of Tannic Acid - 1 part in 1000).

CURVE III.



THE COMBINED EFFECTS OF ACCELERATOR AND RETARDER.

(Conc. of Tannic Acid - 1part in 1000).

CURVE III.

(i) Hardness Tests.

Some of the cakes of plaster appeared to be harder than others so some hardness tests were made. These tests were run on a Olsen U.S. Standard Dorry Hardness Testing Machine. The plaster paste was made up exactely as described under the experimental part of this thesis. After the paste had been prepared it was poured into brass molds, which are a part of the testing machine. When dry, the plaster was removed from the molds in the form of pellets which were 25mm. in diameter and about 5cm. long. The pellets were dried in the laboratory air for three weeks and then put into the Dorry Tester. The test consisted in supporting one of the pellets on a revolving disc under a pressure of 1250 grams. The revolving disc was covered with standard quartz sand of 40 mesh, and the speed of the disc was 28 R.P.M. In testing rock and concrete a run of 1000 revolutions constitutes a test, but the plaster under investigation was so soft that only 500 revolutions were used. The loss in weight of a pellet is supposed to be an index of its hardness.

From Table V it is seen that a pellet of plaster of Paris, without the addition of a compound, lost 38.06% of its weight, while a compound consisting of 80g. plaster of Paris, 80g. of magnesium oxide, made up with 250cc. of a saturated solution of magnesium chloride lost but 9.23% of its weight, or about four times less than ordinary plaster. The other compounds lost a little less than ordinary plaster, with the exception of magnesium chloride which lost a little more.

TABLE V.

Hardness Tests.

Composition	Wt.before run	Wt.after run	Wt.worn away	%worn away
Plain plaster	23.51g.	14.56g.	8.95g.	38.06
43.5g.N/2 K_2SO_4& 43.5g.1:1000 tannic acid.	23.51	16.28	7.23	30.75
43.5gN/8 K_2SO_4& 43.5g 1:1000 tannic acid.	23.58	15.84	7.74	32.82
N/10 NaCl	23.59	14.83	8.76	37.13
N/10 $MgCl_2$	24.34	15.26	9.08	46.96
N/10 K_2CrO_4	22.99	15.47	7.52	32.70
1% Borax	23.50	15.45	8.05	34.25
80g. plaster of Paris; 64g. MgO; 28g.$MgCl_2$; 144 cc. water.	20.73	16.13	4.60	22.19
80g. plaster of Paris; 80g.MgO 250cc. sat. solt. of $MgCl_2$.	30.67	27.84	2.83	9.23

(j) The Effect of Magnesium Oxide and Magnesium Chloride upon Plaster of Paris.

It was found that when 80 g. of plaster of Paris and 80 g. of magnesium oxide were intimately mixed with each other and then added to 250cc. of a saturated solution of magnesium chloride and the resulting paste ground up fine with a pestle and poured into the mold that a cake was formed which was harder than that obtained with ordinary plaster. (See Table V).

When mixed as above described, this compound of magnesium oxide and magnesium chloride retarded the initial set of the plaster by 112 minutes. When hard, the compound had a wax-like surface, and when poured upon a smooth glass plate and allowed to harden and then removed, it was found that the surface which had been in contact with the glass, had assumed an enamel-like gloss. Upon heating some of the enamelled plaster to 50°C. in an oven for a short time it was found that the gloss became wet and could be rubbed off with the finger. The plaster when baked at this temperature and at 150°C. became harder, but after 24 hours it again became as soft as before the baking. The gloss was also slightly soluble in water.
The admixture of soap, with the intention to form calcium stearate, did not decrease the solubility to any extent. When ferric oxide was added to the paste and the mixture then poured upon a glass plate, and allowed to harden, a sheet of plaster resembling polished, red granite was obtained. In all cases the plaster obtained with magnesium oxide, magnesium chloride

and plaster of Paris was a hard mass of which large specimens could be dropped upon the floor without breaking. When the proportions of plaster of Paris was slightly increased over that of magnesium oxide, the plaster also assumed a glossy surface with the glass plate, but the gloss was not permanent, disappearing within a day or two. In all cases before the magnesium oxide was added to the plaster, the former was strongly heated in an iron dish for about an hour in order to drive out the moisture. A cement consisting of magnesium oxide and magnesium chloride, but not with the addition of plaster of Paris is described by Sorel[1] and is known by his name. Compounds of a similar nature as Sorel's cement have been analysed by Bender[2] and Krause[3] with the intention of proving that magnesium oxychloride was formed.

When zinc chloride and zinc oxide were mixed with plaster of Paris in the same proportions and in a similar manner as described for magnesium chloride and oxide, a paste was obtained which set very much quicker than the magnesium compound. The zinc compound was brittle and did not assume the glossy finish as the magnesium compound did.

The time of setting of the magnesium compound could be decreased by the addition of an accelerator as potassium sulphate.

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[1] Sorel, Compt. rend. 65, 102.
[2] Bender, Annalen, 159, 34.
[3] Krause, ibid., 165, 38.

III

THEORETICAL

Recent investigations concerning the setting of plaster of Paris apparently makes it necessary to modify the theory of Le Chatelier in order to explain certain facts which are not adequately accounted for in this theory. Both Cavazzi and Traube have independently and using different processes of reasoning come to the conclusion that in the setting of the plaster there is first a gel-formation from which the interlacing crystals of the dihydrate form. Both investigators have supported their contentions by appropiate experimental evidence.

Furthermore, the action of certain substances upon plaster of Paris is explainable upon the colloidal basis. Thus it has been known for some time that tannic acid precipitates certain colloids as albumen and gelatine. The same acid is also capable of acting as a "peptizing" agent in many instances; as in Acheson's "Deflocculated Graphite" or "Aquadag"; in certain clays and in cements. It would not be unreasonable to ascribe to tannic acid similar properties in the case of Plaster of Paris, although adsorption may play an important part here, as Marc and Wenk[1] have shown that certain dyes have the property of retarding the velocity of crystallization of compounds. In some cases these dyes practically inhibited the formation of crystals. These investigators have shown that this inhibitory action is not due to the mechanically surrounding of the crystals by the dye, but that the crystallization is probably preceded by an adsorption process.

The influence of the anions and acids and their similarity to the Hofmeister series and other series has already been pointed out under the discussion of Traube's investigations.

The action of the colloids as retarders may be explained by assuming that they act as protective colloids, by interfering with the ready growth of the intermatting crystals of the dihydrate of calcium sulphate, although Brann[2] states that the influence of colloids particularly substantiates the assumption that the retardation of the velocity of crystallization of inorganic chlorides and sulphates is an hydration effect.

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[1] Marc and Wenk, Zeitschft. f. phys. chem. 68, 104(1910),
ibid. 61, 385(1908),
ibid. 67, 470(1909),
ibid. 67, 640(1909).

[2] Brann, Jr.Am.Chem.Soc., 40(No.8) 1168-84(1918).

IV

SUMMARY.

1) The time of the initial and final sets of plaster of Paris was determined by means of the Vicat apparatus.

2) By this means it was found that chlorides, sulphates, chromates and nitrates of potassium and sodium are the greatest accelerators.

3) By the same means it was determined that all colloids produce a retardation of the setting of plaster of Paris. Other retarders are borax, boric acid, microcosmic salt and aluminum chloride.

4) Tannic acid, in as small a concentration as one part in ten thousand, produces a deceided retardation of the setting of the plaster. The retarding effects of colloids and tannic acid can be explained by assuming that they act as protective colloids, or that they are adsorbed by the growing crystals of the dihydrate of calcium sulphate.

5) The addition of several accelerators to each other produces no additive effect upon the setting of the plaster.

6) The influence of adding an accelerator plus a retarder to plaster of Paris has been investigated. By decreasing the concentration of the accelerator the retarder gradually assumes the predominant role. This retardation when plotted against the concentration of the accelerator in not a linear but a parabolic function.

7) By mixing equal parts of plaster of Paris and magnesium oxide and adding this mixture to a saturated solution of magnesium chloride a compound is formed which upon setting is harder than ordinary plaster of Paris, and in addition assumes an enamelled surface when poured upon a glass-plate and removed when dry.

V

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